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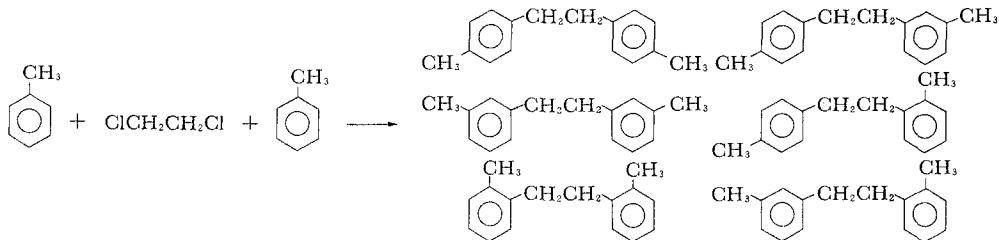
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Friedel-Crafts reaction of toluene with 1,2-dichloroethane was studied. The effective catalysts were aluminium bromide, aluminium chloride, gallium chloride and zirconium chloride. Other Lewis acids examined were inactive. The conversion of 1,2-dichloroethane was completed above 50°C and 40% at 25°C with aluminium chloride. Polycondensation products were mainly formed via disproportionation of ditolylethanes. Relationship between the isomer distribution and the conversion or the reaction time was clarified.

INTRODUCTION

The reaction of 1,2-dichloroethane with toluene in the presence of Friedel-Crafts type catalyst gives a mixture of six isomers of 1,2-ditolylethane as follows¹⁻⁴⁾:



It was described in the previous paper⁵⁾ that these six pure isomers were synthesized and an analytical method of these isomers by gaschromatography was established. In the present paper the effective catalysts for this reaction were searched, and the influence of the reaction conditions on the conversion of 1,2-dichloroethane and on the isomer distribution were also examined.

RESULTS

Catalyst. It is well known that Lewis acids are effective catalysts for Friedel-Crafts reaction.^{6,7)} However, as expected from the structure, the reactivity of 1,2-dichloroethane is so low that it is often used as a solvent of Friedel-Crafts reaction.⁶⁾

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Reaction of 1,2-dichloroethane with Toluene

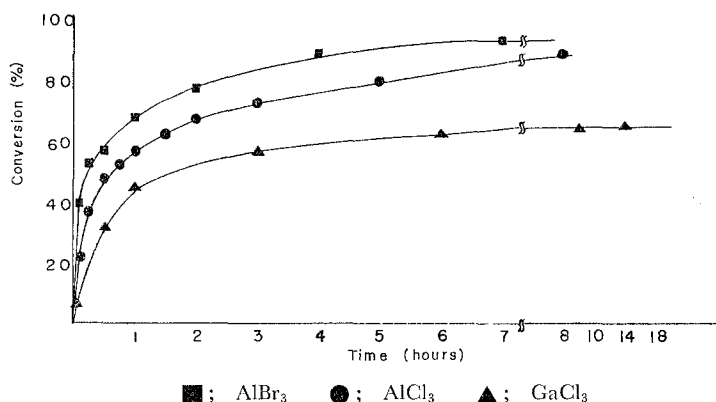
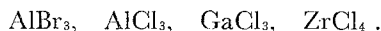


Fig. 1. The relationship between the conversion of 1,2-dichloroethane and the reaction time. [toluene] : [1,2-dichloroethane] : [catalyst] = 1.000 : 0.065 : 0.010. Temp. 60°C.

Among various Lewis acids examined, only few catalysts were effective at a reaction temperature below or near the boiling point of 1,2-dichloroethane (80°C). Catalysts having high activity were as follows:



Catalysts such as $\text{AlCl}_3\text{-CH}_3\text{NO}_2$, $\text{AlCl}_3\text{-C}_2\text{H}_5\text{NO}_2$, FeCl_3 , and TiCl_4 were found to be ineffective under mild conditions, although they yielded trace of ditolylethanes under drastic conditions.*

Other Lewis acids such as SbCl_5 , SbCl_3 , SnCl_4 , $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$, and H_2SO_4 etc. were ineffective under the conditions examined.

Figure 1 shows the relationship between the conversion of 1,2-dichloroethane and the reaction time in the case of AlBr_3 , AlCl_3 , and GaCl_3 catalysts. The order of strength of the catalysts was: $\text{AlBr}_3 > \text{AlCl}_3 > \text{GaCl}_3$. The reaction was almost completed with AlBr_3 and AlCl_3 but with GaCl_3 the conversion stopped at 62% after 6 hours and the reaction didn't seem to proceed further.

Though difference in catalyst activity between AlBr_3 and AlCl_3 was slight, it may be ascribed in part to the difference of their solubility in the reaction mixture.

Influence of reaction temperature on the reaction rate. Influence of reaction temperature on the reaction rate was examined by measuring consumption of 1,2-dichloroethane. As shown in Fig 2, the influence was remarkable. The reaction was completed in 1.5 hours at 80°C and in 5 hours at 70°C. At a room temperature, the conversion was only about 40% in 89 hours, and completion of the reaction required further addition of catalyst.

Polycondensation product. The yield of ditolylethanes was found to decrease from 90~95% to 70~75% based on 1,2-dichloroethane consumed with passage of time. This result suggested that the decrease was due to consecutive reaction of ditolylethanes with 1,2-dichloroethane and toluene (path A in Fig. 3), or disproportionation of ditolylethanes (path B in Fig. 3).

* The reaction was carried out in an autoclave at 220°C.

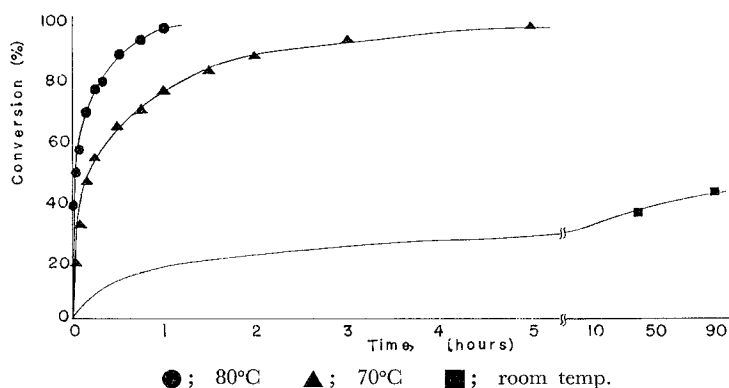


Fig. 2. The relationship between the conversion of 1,2-dichloroethane and the reaction time. [toluene] : [1,2-dichloroethane] : $[\text{AlCl}_3]$ = 1.000 : 0.065 : 0.010.

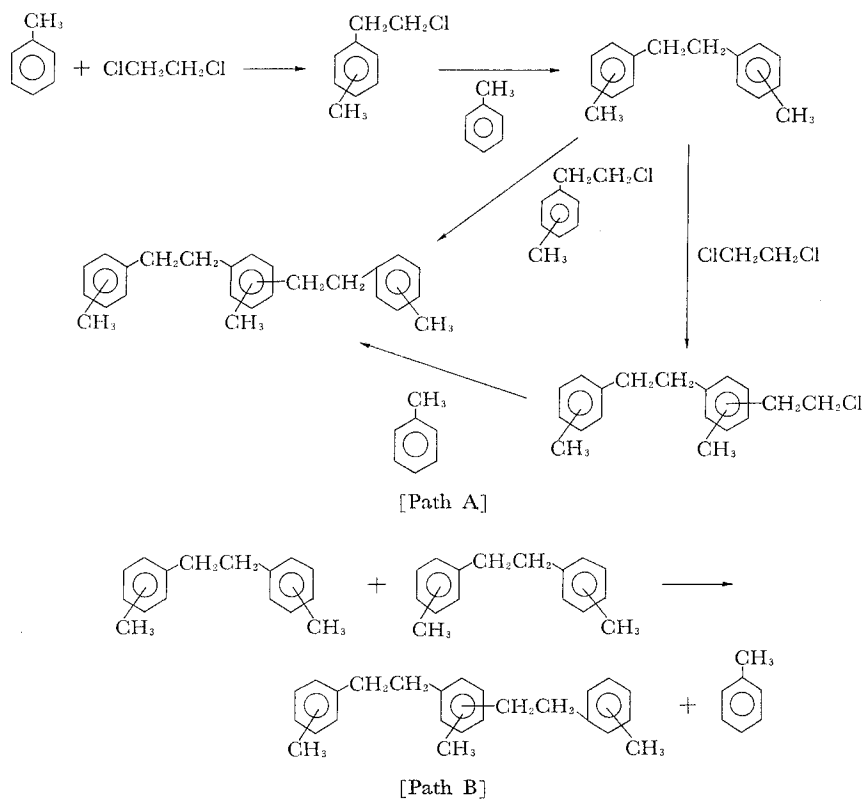


Fig. 3. Path of formation of polycondensation products.

Therefore, after 1,2-ditolylethanes were distilled from the reaction mixture, the residue was chromatographed over basic alumina to give three components* A,B,C.

* They were recrystallized from methanol.

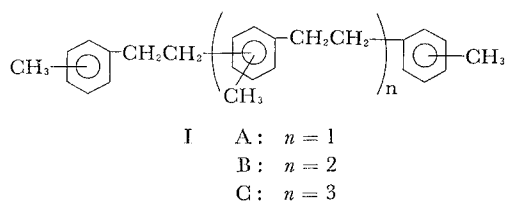
Reaction of 1,2-dichloroethane with Toluene

Table 1. NMR Spectra, Molecular Weight by Mass Spectroscopy, and Elemental Analysis.

Component	NMR spectral data ^{a)}	Molecular weight	Elemental analysis
A	δ : 2.36 ppm, 9H for $-\text{CH}_3$ groups	328	found: C; 91.33 H; 8.77
	δ : 2.83 ppm, 8H for $-\text{CH}_2$ groups		calcd: C; 91.46 H; 8.54
	δ : 6.75 7.20 ppm, 11H for aromatic protons		
B	δ : 2.28 ppm, 12H for $-\text{CH}_3$ groups	446	found: C; 91.24 H; 8.78
	δ : 2.86 ppm, 12H for $-\text{CH}_2$ groups		calcd: C; 91.48 H; 8.52
	δ : 6.63 7.20 ppm, 14H for aromatic protons		
C	δ : 2.22 ppm, 15H for $-\text{CH}_3$ groups	564	found: C; 90.50 H; 8.60
	δ : 2.83 ppm, 16H for $-\text{CH}_2$ groups		calcd: C; 91.49 H; 8.51
	δ : 6.75 7.20 ppm, 17H for aromatic protons		

^{a)} A, B, and C are mixtures of positional isomers, therefore the peaks have showed the complex features near the described values.

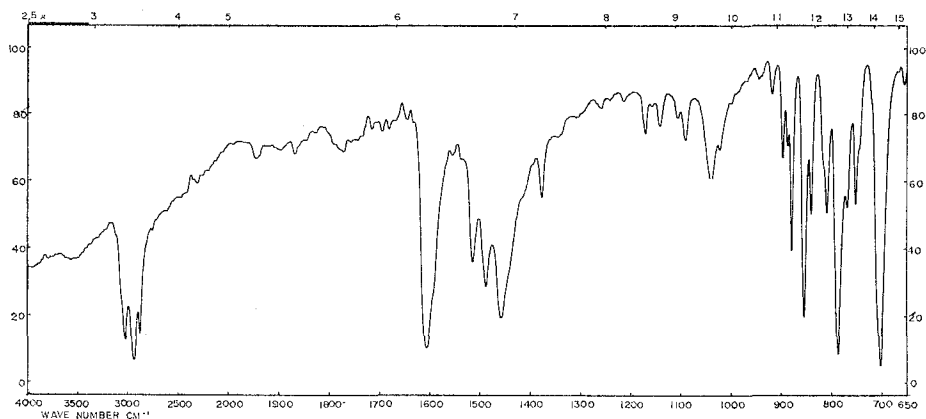
Their spectra of NMR, results of elemental analysis, and their molecular weights by mass spectroscopy were summarized in Table 1. These results show that these components correspond to I_A , I_B , I_C .



Their formations via disproportionation of ditolylethanes are supported by the facts that the yield of ditolylethanes decreased even after dichloroethane was almost consumed and that heating of a mixture of ditolylethanes with AlCl_3 gave I_A , I_B , I_C and toluene.

In Fig. 4 IR spectrum of I_A showed characteristic strong bands (CH out-of plane deformation vibrations) at 703 cm^{-1} , 786 cm^{-1} , 855 cm^{-1} and major substituents at 1,3- and 1,3,5-positions, which fact consistent with considerations that meta-compounds are thermodynamically most stable. Little difference is found between the spectrum of I_A and those of I_B and I_C .

Relationship between the isomer distribution of the products and the conversion or the reaction time. The isomer distribution varied as the reaction

Fig. 4. Absorption spectrum of I_A

proceeded. Figure 5 and 6 show these relationships at 40°C and 80°C, respectively. With increase of the conversion, the relative amounts of mm'- and mp'-compounds increased, but those of oo'- and op'-compounds decreased, and that of pp'-compound was almost constant at the both temperature. The relative amount of om'-compound was almost constant at 80°C but at 40°C once increasing it decreased. These variations may be qualitatively explained by the fact that Friedel-Crafts reaction of toluene

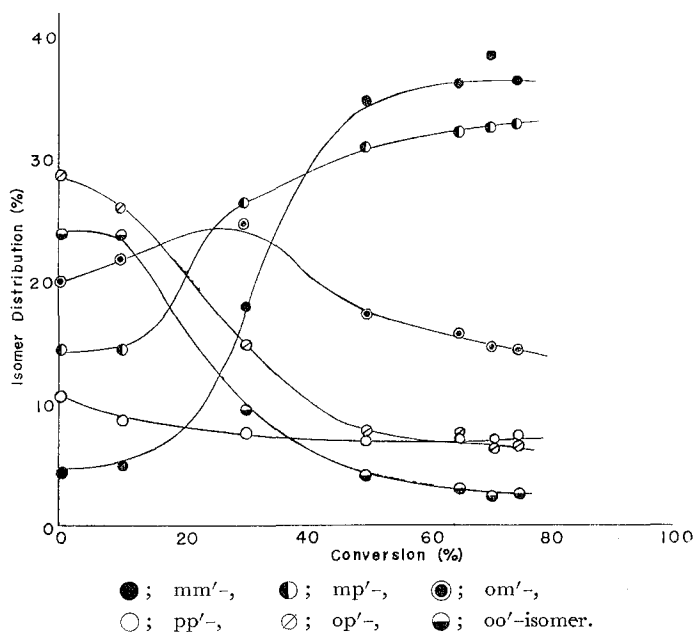


Fig. 5. The relationship between isomer distribution and conversion at 40°C. The experiments were carried out with the following proportions of materials: toluene; 2.00 mole, 1,2-dichloroethane; 0.13 mole, AlCl₃; 0.02 mole.

Reaction of 1,2-dichloroethane with Toluene

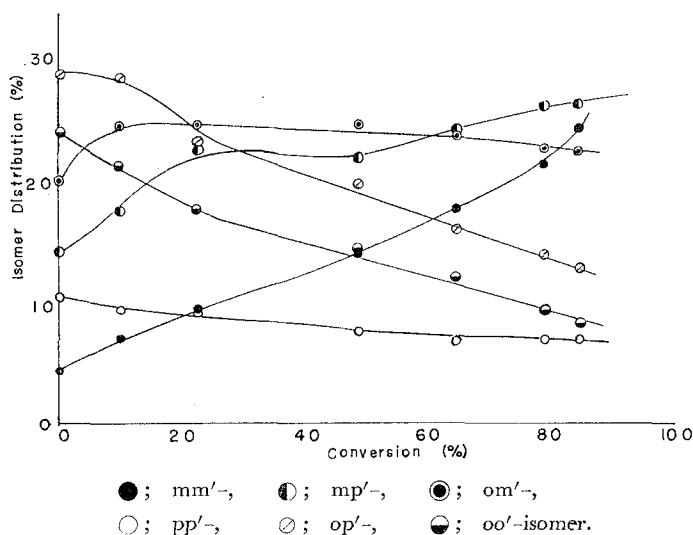


Fig. 6. The relationship between isomer distribution and conversion at 80°C. The experiments were carried out with the following proportions of materials: toluene; 2.00 mole, 1,2-dichloroethane; 0.13 mole, AlCl_3 ; 0.02 mole.

gives a mixture which contains more *o*- and *p*-isomers than *m*-isomer, but it is often accompanied by isomerization of the *o*- and *p*-isomers to the thermodynamically more stable *m*-isomer.

Variation of the isomer distribution between the initial product and final product at the higher temperature was smaller than that at the lower temperature. This result is thought to depend upon the larger activation energy of the reaction of dichloroethane with toluene than that of the isomerization of ditolyethanes.

It is interesting that which contributes more to effect the variation of isomer distribution, intramolecular or intermolecular isomerization, though intramolecular isomerization by 1,2-shift seems to be more important according to the above results. Details on these will be reported in the near future.

EXPERIMENTAL

Materials. Commercial toluene and 1,2-dichloroethane were dried and purified by distillation. AlCl_3 , AlBr_3 , GaCl_3 , ZrCl_4 , other solid metal halides, and liquid catalysts were used without purification.

1,2-Ditolyethanes. These compounds were prepared as shown in the previous paper⁵⁾.

Hydroquinone-di-n-amylether. To sodium ethoxide, prepared from 250 cc of absolute alcohol and 14.0 g of sodium, was added 22.0 g of hydroquinone. This was followed by the addition of 60.4 g of n-amylbromide in small portions. After

heating for 2 hours, the reaction mixture was treated with water, extracted with ether, and distilled. b.p. 128~132°C/0.4 mmHg. m.p. 45°C (from methanol).

Reaction procedure. In a 300-ml. Erlenmeyer flask, fitted with a reflux condenser, a thermometer, and the tube for sampling, were placed 184 g (2 mol.) of toluene and 13.2 g (0.13 mol.) of 1,2-dichloroethane. To this reaction mixture stirred with magnetic stirrer at 60°C, 2.67 g (0.02 mol.) of AlCl_3 pulverized was added. Immediately, the reaction was initiated. 3 ml. aliquots were quenched in dilt. hydrochloric acid periodically, and analyzed after neutralization with sodium bicarbonate, washing with water and drying over anhydrous magnesium perchlorate.

Analysis of the products and the reactant. Hitachi Model F6 gas chromatograph equipped with Golay-type capillary column and hydrogen flame ionization detector was used. Estimation of amount of 1,2-dichloroethane was made in a 45 m. column coated with polypropylene glycol, and sec-butylalcohol was used as a internal standard material. Separation of 1,2-ditolylethanes were made in a 90 m. column coated with butandiol succinate polyester, and hydroquinone-di-n-amylether was used as an internal standard material. The detailed conditions used and I.R. absorption spectra which were simultaneously used for identification have been described in the previous paper.⁶⁾

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